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A paper proposed for presentation at the
1984 Pittsburgh Conference and Exposition on
Analytical Chemistry and Applied Spectroscopy
Atlantic City, NJ
March 5-9, 1984

This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.
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INTRODUCTION

Emphasis on laboratory automation has increased in recent years. The desire to improve analytical reliability, increase productivity, and reduce exposure of personnel to hazardous materials has been fundamental to this increase. The Savannah River Laboratory (SRL), operated by Du Pont for the United States Department of Energy, performs research and development on nuclear materials for the nation's defense and space missions. Development of methods to increase efficiency and safety and to reduce exposure of personnel to radioactive materials is an ongoing process at our site. Robotic systems offer a potentially attractive way to achieve these goals.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

ROBOTIC SYSTEM

Zymark Corporation of Hopkinton, Massachusetts, introduced a laboratory robotic system less than two years ago.[1] Zymark's modular system allows peripheral equipment to be interfaced easily to a robot controller and thus extends the potential utility of the robot. The specific system we are developing consists of the robot, the controller, master laboratory station, power and event controller, specialized hands, vortex stirrers, and a computer interface. These components allow a great amount of versatility in using the robotic system. For a simple procedure, operations can be completely controlled by the robotic system. Where complex calculations are required, interaction with a microcomputer is necessary. In our studies, we have used Commodore PET systems and an IBM 9000 instrument computer.

APPLICATIONS

Free Acid Determination

One application of interest at SRL is the determination of nitric acid concentration in the presence of large amounts of hydrolyzable metal ions. A standard addition technique, developed at SRL, uses 1M potassium thiocyanate as a complexing reagent for the metal ions. The sample aliquot containing ~10 μmol of free acid is dispensed into 10 mL of the potassium thiocyanate complexing reagent. The potential is measured using a combination pH electrode and pH meter set to measure millivolts. An aliqout of standard acid, sufficient to cause a potential change of ~20 mV, is

added to the complexing reagent solution. A second potential reading is then taken. The sample concentration, c_i, is then determined by solving the Nernst equation,

$$E_i = E^\circ + S \log c_i \quad \text{or} \quad \log c_i = (E_i - E^\circ)/S$$

where E_i is the measured potential and S is the Nernst slope (theoretically, 2.303 RT/nF or 59 mV). The slope is experimentally determined in our case. Samples routinely received for analysis by this method may be either radioactive or nonradioactive.

This method has been successfully adapted to the Zymark system interfaced to an independent microcomputer. Figure 1 illustrates the bench setup for the free acid method. Operations performed by the robot at the direction of the controller are: 1) pipetting aliquots of sample and standard; 2) initiating addition and removal of potassium thiocyanate complexing reagent in a stationary sample cell; and 3) initiating microcomputer operation. The microcomputer: 1) tracks the sample being analyzed; 2) provides the sample aliquot size to be used, based on an estimate of the acid concentration present; 3) obtains potential readings from the combination pH electrode through a pH meter/microcomputer interface; and 4) calculates the sample concentration.

Specifically, the operational sequence is as follows:

1. The sample code, lab number, and aliquot size are input into the microcomputer and transferred to the robot through an RS232 interface. The sample code is used as a counter to tell the robot which disposable tip and beaker locations are required for the particular sample being analyzed.

2. The power and event controller activates a peristaltic pump which adds 10 mL of 1M potassium thiocyanate complexing reagent to a stationary sample cell. The cell is mounted on a magnetic stirrer.
3. Using one of two available syringe hands, the robot attaches a disposable syringe tip from the tip rack to the end of the syringe. To verify attachment of the tip, the tip is used to close a contact switch wired to the power and event controller. If contact is not made, the robot will attach another tip.
4. The hand moves to the appropriate sample vial location in the sample vial rack. The volume of sample aliquot initially input into the microcomputer (based on an estimate of acid concentration present) is taken from the sample vial. To aid in quantitative delivery, the syringe hand pauses for 2 seconds to allow the liquid level to become stationary, and an air pocket is withdrawn before and after the liquid aliquot.
5. Since liquid adheres occasionally to the outer walls of the disposable tip, the tip is positioned over a cotton ball loosely placed in a funnel. The robot moves down and in four directions to "wipe" liquid from the tip. The sample aliquot is then added to the stationary sample cell.
6. The robot informs the microcomputer that sample addition has taken place. The microcomputer now begins taking millivolt readings from the interfaced pH meter. Readings that vary less than 0.2 mV over a 15 second interval are considered stable.

7. In the meantime, the used disposable syringe tip has been removed, and a fresh tip has been attached to the proper syringe hand. Attachment of the tip is again verified.
8. The syringe hand moves to a position above the vial containing standard acid. If a stable millivolt reading has not been obtained, the robot waits until the microcomputer has taken the reading. The microcomputer then signals the robot to continue operation. The robot takes an appropriate standard aliquot using the techniques for quantitative delivery listed in Step 4 and adds it to the stationary sample cell.
9. A stabilized potential reading is taken as in Step 6. The microcomputer calculates sample concentration and prints the result.
10. A solenoid valve in-line to a vacuum source is activated by the power and event controller to open, allowing used complexing reagent to be aspirated. More complexing reagent is added to the cell as a flush and this is also aspirated. The system is then ready for the next sample.

Two factors important in dispensing an accurate liquid aliquot were mentioned in Step 4, the use of an air pocket and a pause. During initial use of the robot, it was noted that pipetting only the amount to be dispensed usually left a small amount of liquid in the disposable tip, which was undesirable. By programming the syringe to take a small portion of air initially, a "cushion" of air is available to totally empty the syringe upon dispensing.

Occasionally, a syringe would leak as the robotic arm moved from one location to another. Withdrawing an air pocket after the liquid aliquot has prevented this. Finally, since the syringe stepper motor moves quite rapidly during the liquid withdrawal, the syringe tip remains in the liquid for 2 seconds to allow the liquid level to stabilize.

Operation of the method using standard acid solutions indicate that the relative standard deviation is comparable to that obtained by an analyst (±2.5%, 1σ). Analyses of process sample solutions using the robotic system compare favorably to those determined by an analyst. Table 1 lists comparative values. The time required per determination is about 4 minutes, excluding bench setup time. While this time is comparable to that taken by an analyst, the radiation exposure of the analyst would be greatly reduced because contact time with the sample is decreased.

Chloride and Fluoride Analysis

The standard addition technique described above was also applied to the analysis of chloride and fluoride ions using specific ion electrodes. No major changes were required in the robot or microcomputer programming or in the robotic bench setup. For analyses using the chloride electrode, the diluting reagent is 0.1M sodium nitrate. A reference electrode is also used. For fluoride analyses, a combination fluoride electrode is used. The diluting reagent is a 10% solution containing TISAB III, a complexing reagent manufactured by Orion for use with the fluoride electrode.

Results obtained using standard solutions (Tables 2 and 3) indicate a relative standard deviation (1σ) comparable to that of the free acid analysis.

Gamma Tube Preparation

Another application of interest for the robotic system is the preparation of samples for gamma activity analysis. Many SRL samples must be analyzed for gamma activity. The samples are diluted to an optimum range for gamma activity counting. Automation of this process would free analysts from a monotonous procedure. The bench setup for this is depicted in Figure 2.

Application of the robot is straightforward.

1. Using a syringe hand, a disposable tip is attached from the tip rack. The tip closes a contact switch to verify tip attachment. If the switch remains open, the robot attaches a new tip.
2. The appropriate sample aliquot is taken from the sample vial and is dispensed into a 1-dram glass vial.
3. The remote dispenser is used to add 1M nitric acid diluent from the master laboratory station to the vial.
4. A general purpose hand takes the vial to the capper station, where a screw cap is installed. The vial is placed into a secondary container which is manually capped, and the contained vial is taken to the counting room.

This method has been demonstrated, but actual samples have not been analyzed because the robot has not been placed into a radioactive containment hood as yet. Tables 4 and 5 list the accuracy and relative standard deviation for the hands and master lab station syringes. The volumes dispensed by the syringe hands and syringes on the master laboratory station indicate that the dilution accuracy of this method is quite good, equivalent to that performed manually, and better than the accuracy of the counting method used for analysis. Time required per sample is ~3 minutes, excluding bench setup time.

ADDITIONAL METHODS

Additional applications for the Zymark robotic system include preparation of dilution vials,[2] mounting samples for alpha activity counting, and liquid-liquid extractions for radioisotope separations. The dilution vial operation has already been transferred to our plant process control laboratory. It is designed to fill and automatically cap approximately 10,000 vials per month, each containing 2 or 10 mL of 1M nitric acid. Some of the special devices designed for these methods include magazine dispensers for stainless steel alpha plates and planchets, a tweezer hand to pick up plates, cap dispensers, and a bottle holder for the capper.

REFERENCES

1. G. L. Hawk, J. N. Little, and F. H. Zenie. "A Robotic Approach to Automated Sample Preparation," American Laboratory, June 1982.

2. G. M. Dyches and S. D. Burkett. "Laboratory Robotics Systems at the Savannah River Laboratory." **Proceedings of the 1983 Eastern Analytical Symposium,** New York, NY, (November 16-18, 1983).

TABLE 1

Free Acid Analyses

Sample	Normality Manual	Normality Robot
1	0.31	0.31
2	0.35	0.33
3	0.35	0.30
4	0.05	0.05
5	0.01	0.01
6	0.01	0.01
7	<0.01	<0.01
8	0.070	0.063
9	0.069	0.063
10	1.40	1.49
11	1.42	1.42
12	0.064	0.059
13	0.80	0.83
14	0.82	0.77
15	0.086	0.083
16	0.009	0.009
17	0.009	0.008
18	0.009	0.008

TABLE 2

Chloride Standards

Standard Value, M	Analyzed Value, M	RSD,* %
0.1061	0.1076	1.4
0.0103	0.0104	4.0
0.0167	0.0163	1.0
0.0534	0.0557	1.9
0.0057	0.0055	2.3

* Relative standard deviation

TABLE 3

Fluoride Standards

Standard Value, M	Analyzed Value, M	RSD,* %
0.010	0.009	1.4
0.009	0.009	0.9
0.100	0.091	4.4
0.014	0.014	1.2

* Relative standard deviation

TABLE 4

Syringe Hand Precision

Syringe Size, µL	Aliquot Size Nominal, µL	Aliquot Size Actual, µL	RSD,* %
250	12.5	11.4	3.2
	62.5	59.7	2.1
	125.0	120.8	0.9
	187.5	179.8	0.1
500	25	22.0	0.7
	125	120.0	0.9
	250	244.3	0.3
	375	368.8	0.3

* Relative standard deviation

TABLE 5

Precision of Master Lab Station

Syringe Size, mL	Volume Dispensed, mL	RSD,* %
1	0.9989	0.08
5	4.984	0.15

* Relative standard deviation

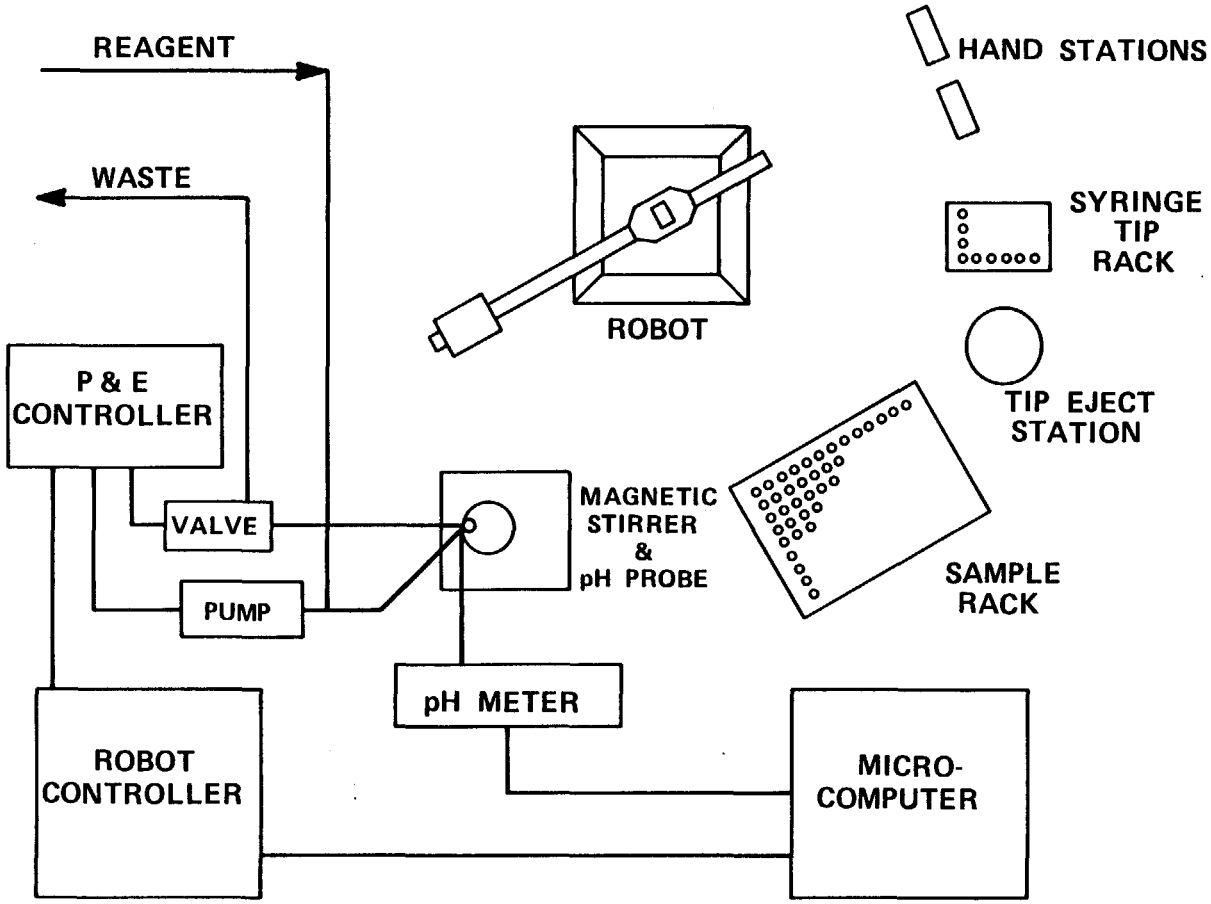

FIGURE 1. Free Acid Determination

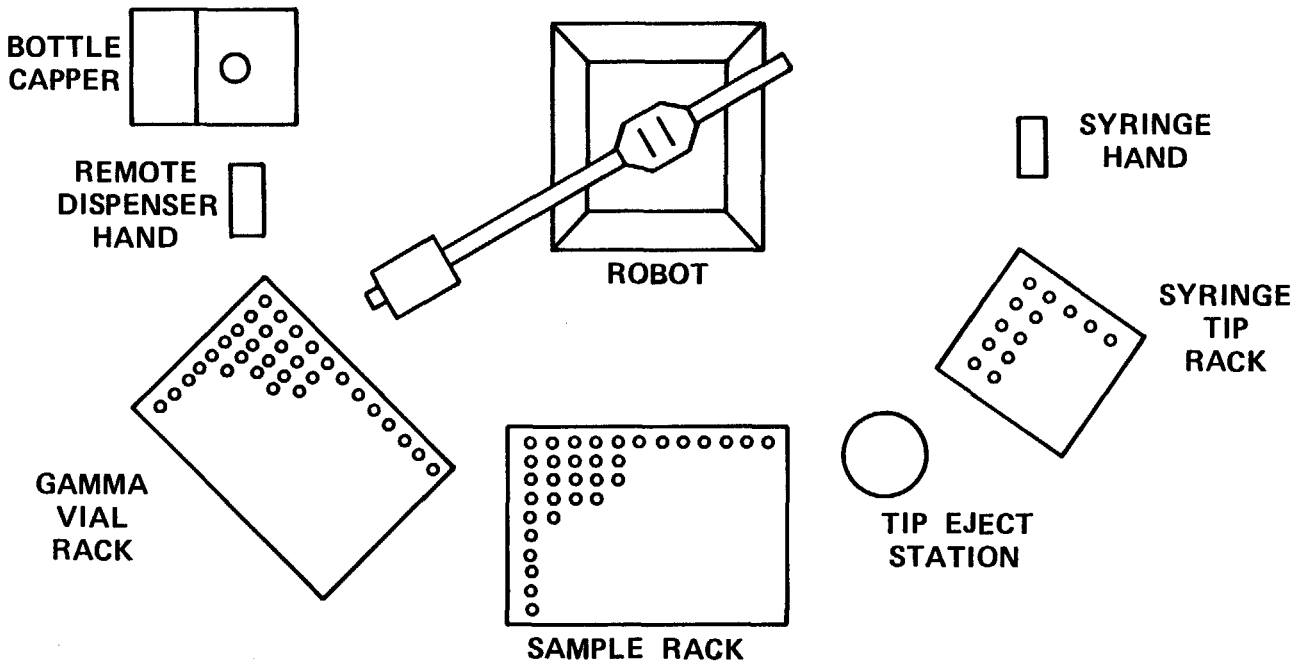

FIGURE 2. Gamma Tube Preparation